Paint and Polymer Analysis and Comparison

1. Scope

The purpose of this analysis is to search submitted evidence for paint and other polymeric materials and compare unknown samples to known paint and/or polymers. Identification of the polymer type may also be included in the analysis.

2. Terms and Definitions

Paint – A suspension of a pigment in an oil vehicle. Any surface coating, that is designed to protect, decorate or both (paint should be called a surface coating).

Coating – A surface coating intended to provide protection, corrosion resistance, aesthetically attractive appearance, or to perform a specialized purpose.

Vehicle or medium – The nonvolatile film former that binds the pigment particles to one another and to the substrate. It is typically a synthetic resin. It is synonymous with binder in high solids and powder coatings.

Lacquer – Fast-drying coating, clear or pigmented, that dries by evaporation of the solvent rather than by oxidation or polymerization.

Varnish – A clear homogenous solution of drying oils and resins in organic solvents. The resins may be natural such as rosin or synthetic such as formaldehyde.

Enamel – Implies a pigmented coating that dries to a hard gloss. It is cross-linked thermosetting resin.

Solvent – Liquids of various types having a function of dissolving the binder and providing a suitable consistency to the coating for application.

Plasticizer – A material incorporated into a polymer to increase its flexibility or workability.

Thermoplastic polymer – A resin that polymerizes without the necessity of heat. If the resin is heated below its decomposition temperature, it softens. It re-hardens upon cooling.

Thermosetting polymer – A resin that can be made to form cross-linkages when baked. It does not soften upon heating.

Binder – Enables the pigment to be distributed over the surface. Binders are synonymous with vehicles.

Pigment – A finely powdered solid that is insoluble in the medium in which it is dispersed. Pigments may impart color or may modify the physical properties of a coating or both. Pigments may be inorganic such as titanium dioxide or organic such as pthalocyanine. Pigments are primarily used to hide the underlying surface.

Effect pigment - flake or platy structures that impart a directional light reflectance, scattering, absorption, or optically variable appearance to the substrate in or on which they are applied. For the purposes of this standard operating procedure, effect pigments are manufactured particles that manipulate light in such a way as to create a color change or a sense of “depth” to the topcoat. Effect pigments are typically coated titanium oxide particles.

Metallic flake - small particles of metal, commonly aluminum, dispersed in the topcoat to produce specular reflection creating a metallic-looking finish.

Mica flake – small platelets of mica dispersed in the topcoat to produce a pearlescent effect to the finish.

Dye – A dye is soluble in the medium in which it is dispersed.

Latex – A suspension of pigment in a water based emulsion of any of several resins (i.e. Acrylic polymers, vinyl polymers or styrene-butadiene polymers). After polymerization, latex is a solid dispersed in water and is not a true emulsion, but it is often referred to as one.

Dryer – A material that promotes or accelerates drying, curing or hardening of oxidizable coating vehicles. The principle driers are metal esters of mono-carboxylic acids and are called soaps.

Extender – A low-cost inorganic pigment used with other pigments to modify gloss, texture, viscosity and other properties and to reduce the cost of the final product. Extenders cannot be used without other pigments.

Resin – A material capable of being converted from a solution into a self-sustaining film. It may be applied to a polymer that is a binder for coatings and plastics.

Shellac – A solution of the excretion of certain insects typically dissolved in alcohol. It is employed as a sealant, an adhesive or an insulating varnish.

Nitrocellulose paints – Nitrocellulose lacquer, often mistakenly referred to as "Nitro" was used as a finish on guitars for most of the 20th century and is still used on some current applications. Manufactured by (among others) Dupont, the paint was also used on automobiles sharing the same color codes as many guitars, primarily Fender. Nitrocellulose lacquer is also used as an aircraft dope, painted onto fabric-covered aircraft to tauten and provide protection to the material.

Suspending agent – A suspending agent helps reduce the sedimentation rate of particles in suspension. These are insoluble particles that are dispersed in a liquid vehicle. The suspending agent works by increasing the viscosity of the liquid vehicle and thereby slowing down settling.

Non-aqueous dispersion enamels – These enamels consist of a non-aqueous continuous phase comprised of a mixture of organic liquids, one which is an alcohol, when applied to a suitable substrate, dries to produce a clear, glossy film.

Water-based dispersion enamels – These enamels are dispersed in water and are safer because they do not produce potentially harmful vapors.

Primer – A primer is a preparatory coating put on materials before painting. Priming ensures better adhesion of paint to the surface, increases paint durability and provides additional protection for the material being painted.

Acrylic lacquer – A lacquer that is made up of an acrylic polymer resin is a thermoplastic resin manufactured by the polymerization of various monomers such as acrylic acid, methacrylic acid and esters of these acids. Used in durable coatings, finishes, waxes and adhesives.

Acrylic enamels – Acrylic enamel is a single stage paint (no clearcoat) that provides good durability and protection. This paint was used for years as a tougher alternative to factory price. Acrylic enamels can be sprayed with or without a hardener. Hardener increases the paints durability and shine while it decreases the dry time.

Alkyds – Alkyd coatings are a class of polyester coatings derived from the reaction of an alcohol and an acid anhydride hence the term alkyd and are the dominant resin or "binder" in most "oil-based" coatings sold to the consumer market.

Layer structure – The layer structure consists of a primer layer, a paint layer and typically a clearcoat layer.

Texture – The physical appearance or character of paint at both the macro and microscopic levels.

Color – Color derives from the spectrum of light (distribution of light energy versus wavelength) interacting in the eye with spectral sensitivities of the light receptors.

OEM – Original Equipment Manufacturer.

3. References

ASTM E1610 *Standard Guide for Forensic Paint Analysis and Comparison*, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA.

ASTM E2809 *Standard Guide for Using Scanning Electron Microscopy/X-ray Spectrometry in Forensic Paint Examinations*, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA.

ASTM E2937 *Standard Guide for Using Infrared Spectroscopy in Forensic Paint Examinations*, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA.

David A. Crown, The Forensic Examination of Paints and Pigments, Charles C. Thomas Publisher, 1968.

Brian Caddy, Forensic Examination of Glass and Paint: Analysis and Interpretation, Taylor and Francis, 2001.

4. Examination Procedure

4.1. Evidence types

Evidence that is associated with hit and run cases, homicide, property damage, burglary, and theft can include, but is not limited to: vehicles, paint samples from a crime scene or item, painted vehicle parts from a scene, clothing from subject(s) and victim(s), items with a paint transfer such as tools, vehicle parts, mailboxes, spray paint cans, safes, bicycles and any known painted items. Other plastic and polymeric materials may also be analyzed, identified, and compared with this procedure.

4.2. Reagents and Chemicals

Epoxy or plastic mounting medium

4.3. Procedural and Chemical Precautions

Refer to the TBI Safety Manual for general safety requirements and hazard information regarding the use of reagents, solvents, and overall safety guidelines.

When carbon coating samples, the carbon rods should only be observed using goggles rated for welders and cutters. The goggles conform to ANSIZ87.1.

When filling a dewer flask with liquid nitrogen to be used in the carbon coater, Fourier Transform Infrared Microspectrometer (FTIR), and the Scanning Electron Microscope/Energy Dispersive System (SEM/EDS), protective clothing shall be worn. This includes cryogenic gloves, full-face shield and laboratory coat.

Protective attire, including laboratory coat, mask, gloves and eye protection should be used when working with clothing and/or bloodstained items.

Decontamination of a scientist's work area should be performed after each use, but shall be done after analyzing bloodstained items.

Hazardous chemicals shall be used in a chemical fume hood.

When necessary, consult section and laboratory Material Safety Data Sheets (MSDS) regarding any chemical used in the Microanalysis section.

Drying of victim clothing from a hit and run case shall be performed in a fume hood.

4.4. Limitations

The amount and/or condition of the paint sample or smear may limit the number of analytical techniques available and may limit the conclusion reached.

4.5. Procedure

Document submitted samples according to *Microanalysis Quality Assurance Policy*.

The submitted evidence may be photographed for case file documentation.

4.5.1. **Clothing Analysis**

4.5.1.1. Wet clothing

Blood stained or wet evidence should be transferred to the Microanalysis unit or placed in the triage room immediately upon receipt into the laboratory. The evidence should be maintained in its original packaging under a hood and allowed to dry. The packaging may be opened to speed the drying time. If the evidence will not dry in its originally packaged condition, the evidence may be spread out on clean catch paper under the hood and allowed to dry. Do not hang up clothing as this can risk the loss of transfer type evidence. This catch paper must be searched for paint evidence along with the clothing. If the evidence is to be analyzed by another unit, appropriate precautions shall be taken to preserve other evidence types. If other evidence will be lost or damaged by these procedures, modifications may be made after consultation with other analysts. Document changes in case notes.

4.5.1.2. Scraping Evidence Clothing

Suspend item over clean catch paper. Scrape the item with a long spatula to dislodge debris from the item. If the items have been submitted in separate bags, each item may be scraped separately. However, if the items are received in the same package they may be scraped collectively.

Collect the debris in a labeled container.

If appropriate to the case, the item should be examined for paint smears embedded in the fabric. Document and collect a cut out of the smear for further examination.

Paint samples recovered from the scene should be examined in its original packaging or transferred to an appropriately labeled container.

Known paint samples should be examined in its original packaging or transferred to an appropriately labeled container. A representative known paint sample should be taken from painted items submitted as evidence. The sample shall be retained in an appropriately labeled container.

Items with a possible paint transfer shall be searched visually and/or microscopically over catch paper. The paint transfer should be removed, if possible, and retained in an appropriately labeled container. The catch paper shall be searched for paint evidence if necessary to find additional evidence.

4.5.2. **Microscopic examination**

Microscopic examination of paint and polymer evidence shall be performed with a stereomicroscope or video microscope (Keyence). The unknown or question exhibit(s) shall be evaluated for suitability for analysis before the evaluation of the known exhibit(s). In some cases, it may be necessary to preliminarily evaluate the known exhibit(s) in order to obtain appropriate evidence from the unknown exhibit(s) for further analysis.

The paint/polymer specimens shall be separated from debris scraped from evidence and placed in an appropriately labeled container.

Paint specimens should be examined on all sides (top, bottom and edges).

Microscopic examination of each specimen shall include, if appropriate to the sample, documentation of the following:

Color – the color of each layer within the sample will be noted using reflected light. Unknown and known samples may be compared side-by-side to assess any color differences.

Appearance – determination of metallic, non-metallic, or pearlescent finishes or other effect pigments. Describe the appearance of the flakes.

Texture – surface texture noted will include features such as gloss, coarseness, and roughness.

Physical structure – Response when the specimen is probed including pliability, brittleness, and resiliency.

Layer structure – paint samples will be oriented in such a manner as to allow the examiner to observe the edge and document the layer structure. The features observed are:

number of layers
the color sequence of the layers
thickness of layers
texture and appearance of the layers
visual appearance of a possible repainted finish

Foreign matter – it will be noted if any foreign matter is embedded in any of the layers.

Unknown and known samples may be compared side-by-side to assess any differences.

If meaningful differences in the observed physical properties are determined, report that the unknown and known paint samples are inconsistent.

If no meaningful differences are observed, further analysis shall be performed.

4.5.3. **Fourier Transform Infrared Spectrometer with Microscope Analysis (FTIR)**

The FTIR microscope analysis is used to analyze and compare the organic composition (typically binder) of the unknown and known paint/polymer samples. The unknown samples shall be analyzed prior to the known samples.

Each layer of the unknown and known paint samples shall be analyzed separately. Multiple samplings should be prepared in order to assess any variability in the paint layer. Samplings may be prepared by one of the following techniques:

Using a scalpel blade, separate each layer by cutting and slicing each layer. Press each layer separately with a KBr press. Individual layers may be mounted for analysis by attaching the layers to tape adhering to a FTIR sample holder, placing on a salt plate, or mounting in a diamond cell.

Embed the paint chip in a plastic medium. After curing, obtain thinly sliced cross-sections of the sample using the microtome. The thin sections may be further pressed in a diamond cell or a KBr press. The sections will be suspended on tape adhering to a FTIR sample holder, analyzed on the diamond cell, or placed on a salt plate.

Place paint chip on glass slide. Place another glass slide on top of chip exposing part of the sample. Slice the paint chip along the glass edge, slightly moving the top slide. Slice again to attain a cross section. Press, if necessary, in a diamond cell or a KBr press. The sample will be mounted for analysis by attaching the layers to tape adhering to a FTIR sample holder, placing on a salt plate, or mounting in a diamond cell.

Acquire a minimum of 50 scans for each sample analyzed and a minimum of 50 background scans. Other instrument parameters are printed on the spectrum printout. Acquire a spectrum of a polystyrene standard for each day of case analysis and retain in the case file. Observe the following peak wavenumbers: 3082, 3060, 2849, 1943, 1601, 1028 and 906. The bands will not vary more than +/- 2 wavenumbers. Acquire spectra of the samplings from each layer in both the unknown and known samples.

Identification of the paint layer binders may be performed, but it is not necessary for paint comparisons. The examiner may use spectral libraries on the instrument, peak tables, and/or other reference materials in the laboratory to add in the identification process. Identification of polymeric materials should be performed by comparing the generated spectrum to spectral libraries on the instrument. The use of peak tables and/or other reference materials in the laboratory may also be useful.

Compare spectra generated within each layer of the known paint samples to determine the variability of the paint within the layers. Compare the replicate generated spectra for each layer of the unknown paint samples to the known paint by examining peak position and relative peak intensities. If the peak position and intensities are within the established variability of the known, the spectra are consistent with one another, and a scanning electron microscope/energy dispersive spectrometer (SEM-EDS) comparison is then performed. If there are meaningful differences observed between the unknown and known spectra, report that the unknown and known paint samples are inconsistent.

4.5.4. **Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS)**

The SEM/EDS allows the paint sample to be magnified and analyzed by X-rays to reveal the inorganic composition (typically pigments and extenders) of the paint or polymeric material.

If the paint layers have not been separated, then one of the following is necessary before analysis by SEM/EDS.

Separate layers by any of the three procedures listed under FTIR comparison. Place the individual layers or the thin cross-sections of the paint samples on an aluminum SEM stub using either carbon conductive tape or tabs.

Set the paint chip on edge, perpendicular to the SEM stub using either carbon conductive tape or tabs.

If the paint layers have been separated for FTIR analysis, these samples should be attached to an aluminum SEM stub using either carbon conductive tape or tabs. If the paint layers were attached to tape on the FTIR sample holder, this tape with samples may be pulled from the FTIR holder and stuck directly to the SEM stub with carbon conductive tape or tabs. View under stereoscope to assure samples are well adhered to the carbon medium.

Place the stubs into the carbon coater chamber. Place the chamber under vacuum and coat with a thin film of carbon to increase electrical conductivity. This process is outlined in the Denton carbon coater instructions and is also available in step-by step instructions next to the coater. Return the chamber to atmospheric pressure and remove the stubs.

Bring the SEM/EDS chamber to atmospheric pressure and load sample stubs into the chamber. Return the chamber to high vacuum.

Optimize the SEM/EDS. This optimization is to be run with each batch of sample stubs. Optimization will be performed using the parameters below. Cobalt will be the calibration element and is retained on a standard reference stub in the SEM/EDS chamber. The reference material is the MAC Reference Standard for X-ray Microanalysis #7019. Using the *Analyzer*, *Point and ID*, or *GSR* software, open a project to store data. On the SEM, once the calibration element is displayed and in proper focus, the acquisition can begin with the EDS software. The SEM spot size should be set to approximately 25% (for the EVO 50 and EVO 10) or 30-40% (for the Leo 1450) dead time. The spot size can be changed by selecting the 'gun' folder. The acquisition will then be stopped and restarted and allowed to acquire for the full time. Using the EDS software, select 'measure' and note the value displayed. The value should be 100% +/- 3%. If not within the 3%, repeat the optimization. Generate a spectrum and record the measured value on the spectra. These results are stored in each case file. The instrument parameters are printed and shall be placed in each case file. These are the operating parameters for the SEM/EDS:

Livetime (sec)	50-100
Accelerating Volt.	20 - 25 KeV
Process Time	2-5
Working distance	8.5mm (EVO10 and EVO50) or 15 mm (LEO 1450)

Using either/or both secondary and backscatter detectors locate each layer and analyze. Acquire multiple spectra of each layer as case notes.

Compare the replicate acquired spectra of each layer of the unknown paint samples to the replicate acquired spectra of each layer of the known paint samples by examining peak position and relative peak intensities. Also identify each element represented by the acquired spectra. If meaningful differences are observed between the unknown and known spectra, report that the unknown and known paint samples are inconsistent. If no meaningful differences are observed and the same elements are represented, report that the unknown and known paint samples are consistent.

4.5.5. Association Significance Interpretation

4.5.5.1. Comparison of unknown paint/polymer samples to known paint/polymer samples may be consistent or inconsistent with respect to the following:

- color
- texture
- type
- layering sequence
- binder composition
- pigment composition

4.5.5.2. If no meaningful differences are observed in all observed and measured properties, the unknown paint is determined to have come from the same source as the known paint or from a different source with identical properties.

4.5.5.3. The following source factors could increase the significance of an association

Unusual physical and/or chemical features (e.g., surface contamination or damage)
Cross transfer of paints between two unrelated surfaces
Transfer of multiple different types of paint from multiple surfaces
Paint formulation applied for other than its intended use (e.g., architectural paint applied to a vehicle)
Paint with a known limited population
Increased number of layers
Unusual layer sequence where sequence order is typically controlled/mandated/deliberate

4.5.5.4. For automotive paint, the following source factors could increase the significance of an association.

Repair during manufacture [original equipment manufacturer (OEM) repair]
Aftermarket refinish– number of layers and characteristics of the refinish affect association significance
Non-automotive paint layer within a layer system
Refinish layer(s) that change the topcoat color of the vehicle

4.5.5.5. For architectural paint, the following source factors could increase the significance of an association.

Multiple layers of various colors
Presence of inclusions, contaminants, or soil
Spray paint layer within a layer system

4.5.5.6. The following source factors could decrease the significance of an association

Limited number of analytical techniques used in the comparison
Limited number of features available for comparison

Condition of samples (e.g., mixed smears, contamination throughout the transferred material, minute sample amount)
Minor physical or chemical differences between items being compared that could be a result of sample heterogeneity, contamination of the sample(s), or having a sample of insufficient size to adequately assess the homogeneity of the entity from which it was derived
Circumstances that increase the possibility of a random association (e.g., the suspect is a house painter and the material in question is an architectural paint)

4.5.5.7. Association Types

There are three levels of association that may be used in reporting consistent paint results.

a. Association with Highly Discriminating Characteristics
   OEM automotive system with at least one aftermarket basecoat or primer layer above the original clear coat
   OEM automotive system with a factory repair that changes the topmost basecoat color (i.e., the original basecoat color differs from the repair basecoat color)
   OEM automotive system with three or more factory repairs (i.e., three or more additional same-colored basecoats)
   Architectural paint system with two or more different colored layers or three or more white layers of differing chemistries
   Automotive system with architectural paint present

b. Association with Discriminating Characteristics
   Association of paint in which the typical analysis scheme was performed on mass-produced materials that have numerous features for evaluation (e.g., four-layered OEM automotive paint)
   OEM automotive paint system
   OEM automotive paint system with a factory repair of the same basecoat color and layer sequence (e.g., one or two basecoat/clearcoat sequences above the expected OEM layer system)
   Single-layered, colored, non-automotive paint
   Architectural paint system with two white layers of different chemistries

Aftermarket refinish clearcoat and basecoat

c. Association with limitations
Smears rather than chips (one or two layers or a mixture)
No elemental analysis performed
Partial transfer of an OEM automotive paint system (e.g., chips containing clearcoat or basecoat only)
Single-layered paint having limited discrimination studies and/or product manufacturing distribution information (e.g., yellow tool paint)

See Reports for example wording of result reports.

4.6. Instruments and Equipment

Catch paper, large spatula
Stereomicroscope
Video Microscope (Keyence)
Petri dishes, small and large
Forceps, scalpel blades, probes, tape and clean scissors
KBr Press apparatus
Fourier Transform Infrared Spectrometer with microscope
Glass slides
Microtome
Epoxy embedding medium, embedding molds
Scanning Electron Microscope, Energy Dispersion Spectrometer
Aluminum Stubs
Carbon conductive tapes and/or tabs
Vacuum carbon coater and accessories
Photographic equipment with accessories
Diamond cell
Salt plates (Kbr, AgCl, etc.)

5. Measurement Traceability

NIST certified polystyrene standard
NIST certified Ni standard
NIST certified Co standard
NIST certified reference filter set

6. Reference Materials

Standard polyethylene
P.D.Q. Automotive Paint Software

7. Reports

The following are possible results concluded from the examination:

Microscopic examination of the paint in this exhibit revealed the following layering sequence: (this will be followed by a list of layers including color and some appearance descriptors).

If the analysis of the paint reaches the level of Highly Discriminating Characteristics: Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be consistent with respect to color, texture, type, layering sequence, binder composition and elemental composition. Analysis also revealed (state the condition from 4.5.5.7.a. that is highly discriminating). Therefore, the unknown paint came from the known paint source or another source with these identical properties. (For vehicles) Due to these properties it is unlikely that another vehicle painted in the same manufacturing plant at approximately the same time would have all of these distinctive properties. Any other vehicle painted in this distinctive manner would also have to be damaged and missing paint to be considered a source of the unknown paint samples. (For Architectural) Due to these properties it would be unlikely that another location would have these distinctive properties. If another location had the exact same paint history, it would also have to be damaged and missing paint to be considered a source of the unknown paint samples.

If the analysis of the paint reaches the level of Discriminating Characteristics: Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be consistent with respect to color, texture, type, layering sequence, binder composition and elemental composition. Therefore, the unknown paint came from the known paint source or another source with these identical properties. (For vehicles) This result would include any vehicle produced at the same manufacturing plant using the same paint system. It should be noted that this analysis will typically distinguish between paints from different manufacturing plants. (For architectural or painted objects) This result would include other paint sources manufactured to the same specifications as the known paint. It should be noted that this analysis will typically distinguish between paints from different manufacturers.

If the analysis of the paint reaches the level of Limiting Characteristics:

Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be consistent with respect to (list any combination of the six properties). Due to (state reason from 4.5.5.7c.), the analysis and comparison were limited. Therefore, the unknown paint cannot be eliminated as having come from the known paint source.

Microscopic and instrumental analysis and comparison of the unknown paint sample to the known paint sample revealed them to be inconsistent with respect to (list characteristics). Therefore, the unknown paint samples did not come from the source represented by the known paint sample.
(For Vehicles it may be added) It should be noted that some vehicles may be painted with different paint systems on different panels of the same vehicle. Upon submission of additional paint samples, further analysis may be performed.

Analysis of this exhibit did not reveal the presence of any paint for comparison.

Examination of this exhibit did not reveal any paint transfers for analysis.

Microscopic and instrumental analysis of the plastic material revealed it to be (state the type of polymer identified).

Microscopic and instrumental analysis and comparison of unknown plastic with known plastic revealed them to be consistent with respect to color, texture, and polymer type. Therefore, the unknown plastic could have come from the source represented by the known plastic or another plastic source with these identical properties.

In the case of cross transfers or multiple transfers, a statement may be added to indicate an increased significance due to these transfers.

The wording of these results may vary due to the circumstances of the particular case.